Scripps CO_2 program atmospheric CO_2 data from ship and ice-floe flasks from campaigns spanning 1957-1984

Lynne Merchant
Ralph Keeling

October 2024

Introduction

This document provides supporting information for data files containing atmospheric CO_2 mole fraction measurements from flasks onboard ships and on ice-floes from 35 campaigns spanning the years 1957 to 1984 and analyzed at the Scripps Institution of Oceanography in the group of C. D. Keeling.

Data files containing all the results

flav_all_cruises.csv - Contains flask CO_2 averages for all campaigns listed in Table 1, i.e. averages of all retained measurements on an individual flask. One or more measurements were made on each flask sample. Flagging of accepted values is included.

fldav_all_cruises.csv - Contains flask CO_2 date-time averages for all campaigns listed in Table 1, i.e. averages of multiple flasks collected concurrently at the same date and time where the times are within a window of 10 minutes. Here there can be more than one average on a given date since flask replicates were occasionally collected more than once a day. Flagging of accepted values is included in the file.

Subsets of these flask data have been used in publications by Bolin and Keeling (1963), Keeling et al. (1984c), Keeling et al. (1989a, 1989b), Keeling et al. (2011) and Weiss (1992) and in unpublished internal reports Keeling (1984a) and Keeling et al. (1986b). Tabulations of CO_2 flask averages from flasks sampled from 11 ship campaigns and an ice floe campaign were provided previously in the internal Scripps report Keeling et al. (1986b). In many of these earlier reports, only derived products (e.g. monthly averages) were provided.

Here we update the CO_2 flask data previously published and in internal reports with several refinements described below. We also provide data from additional 15 previously unreported ship campaigns with the same refinements. This report tabulates individual flask CO_2 values for 35 campaigns. See Table 1 for a list of all the campaigns included in this report and annotations indicating the use of a campaign's data in a previous publication or internal report. Figures 1 and 2 show the data for all campaigns on a single plot as a function of time.

This report incorporates the following refinements:

(1) Updating of CO_2 mole fractions to the x08A calibration scale. To update the data previously provided in the 1986b report, we applied revised corrections per Keeling (1987), and we applied a consistent correction for 2 L sampling flasks, which had previously only been applied to data for a subset of the campaigns. The corrections from Keeling (1987) resulted in changes for individual flasks between 0.08 ppm lower to 0.24 ppm higher.

(2) Incorporation of data from campaigns that were not included in previous publications and internal reports. These additional data sets were found in digital form on the group data server in a directory of data used in the Keeling et al. (1986b) ship report.

(3) Inclusion of finer-grained information about sampling times. The flav_all_cruises.csv file contains not only sampling date, but also sampling time, and these date-time values are expressed in UTC. The Keeling et al. (1986b) tabulation listed data only by local date, but not time.

(4) Inclusion of averages over replicates of flasks collected at the same date and time in fldav_all_cruises.csv. The Keeling et al. (1986b) tabulation listed data for individual flask averages, but did not provide averages over replicates from the same date and time.

(5) Full documentation of data quality flags used previously in support of the above reports or publications.

(6) New data quality flags based on an update to data screening methods.

(7) Inclusion of the 'J index' in the flav_all_cruises.csv file where the 'J index' is a provisional manometric mole fraction scale linear with the APC analyzer measurement response. The 'J index' is the CO_2 value before a series of measurement and flask corrections are applied to get the CO_2 values on the calibrated X08 scale.

Table 1. Ship and ice-floe campaigns included in this report

Data set Abbrev.	campaign Name	Dates (YYMMDD)	Prev. Pub[1]	Latitude	Longitude
DWN	DOWNWIND	571027 to 571223	a	48S - 17.5N	144.5W - 72W
LIM	LIMBO	600518 to 600625	a	23N - 29.8N	139.2W - 117.7W
TET	TETHYS	600618 to 600818	a, d, e	4.9S - 30N	162.3W - 120.6W
MON	MONSOON	600827 to 610418	a, d, e	63S - 33.6N	178W - 180E
RIS	RISEPAC	611029 to 620204	a, d, e	17S - 31N	147.2W - 100.8W
HIX	HILO campaign	620325 to 620506	a, d, e	21.3N - 30.5N	153.2W - 119.7W
LUA	LUSIAD (ARGO)	620519 to 630813	b	51.1S - 35.1N	179.5W - 137.7E
ELT	ELTANIN	620712 to 720314	d, e, f	77.7S - 34.9N	179.3W - 179.3E
PRO	PROA	620808 to 620829	a, d, e	10.4S - 17.5N	172.9W - 0.2W
LUH	LUSIAD (HORIZON)	630106 to 630204	d, e	16S - 20.2N	180W - 174.8E
EQl	EQUALANT I	630219 to 630316		1.5S - 1.5N	30W - 27.4W
EQ2	EQUALANT II	630803 to 630815		15S - 12.5N	26.5W - 24.7W
CRR	CARROUSEL	640617 to 640815		35S - 20N	115W - 76.9W
ARL	ARLIS II	610820 to 640915	d, e	74.4N - 88.7N	178W - 180E
EST	EASTROPAC	670126 to 680328	d, e	20S - 27.8N	126.1W - 96W
NOV	NOVA	670424 to 670911	d, e, f	34.1S - 34.4N	179.2W - 179.2E
OCE	OCEANOGRAPHER	671012 to 671108		37.7S - 25S	180W - 174.8W
ICA	ICE FLOE A	570923 to 580322	f	83.7N - 85.4N	169.6W - 153.5W
ICB	ICE FLOE B	571020 to 571222	f	80.3N - 81N	114.8W - 109.1W
NAT	NATCHIK	620818 to 620912		64.5N - 71.4N	169W - 156.5W
TT3	T-3	620616 to 620830		76.6N - 78.4N	170.2W - 163W
PL1	PLEIADES	760430 to 760615		3.9S - 30.3N	116.4W - 80.3W
PL2	PLEIADES	760430 to 760615		3.9S - 30.3N	116.4W - 80.3W
IND	INDO-MED	771108 to 790315		64.2S - 35.7N	103.7W - 110.6E
HUD	HUDSON - 82	820228 to 820405	g	56.3N - 78.1N	15.2W - 70E
FGE	FGGE	790206 to 800614	c, d, e	17S - 21N	158W - 150W

TTO	Transient Tracers in the Ocean / North Atlantic Survey (TTO/NAS)	801018 to 811018	g	15.1N - 78.5N	74.5W - 78.5E
TAS	Transient Tracers in the Ocean / Tropical Atlantic Survey (TTO/TAS)	821212 to 830216	g	8.4S - 16.3N	49.9W - 28W
OCA	Ocean Air Program Comprised of 7 campaigns: NEW HORIZON (N01, N02, N03, N04), PARALLA (P01, P02) AKADEMIK KOROLEV (AKA)	830603 to 840124		30S - 46.1N	155.1W - 118.1W
STN	U.S. Weathership 'N'	620810 to 631015	d, e	30N	140W - 139.6W

[1]Previous publications and internal reports using these data: a. Bolin and Keeling (1963), b. Keeling (1984a), c. Keeling et al. (1984c), d. Keeling et al. (1986b), e. Keeling et al. (1989a and 1989b), f. Keeling et al. (2011), g. Weiss 1992

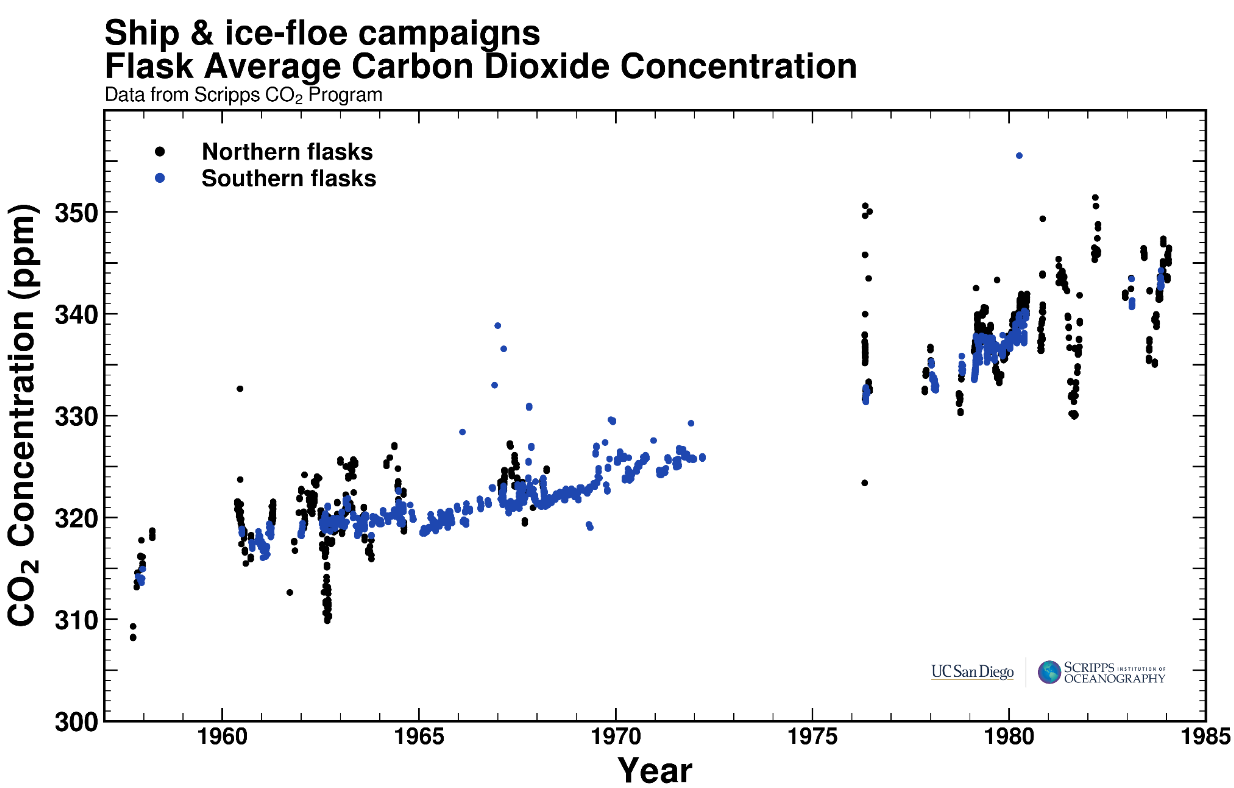

Figure 1. Flask average CO_2 concentrations for all campaigns in this report on x08A scale with accepted flag values and within 3 std of mean.

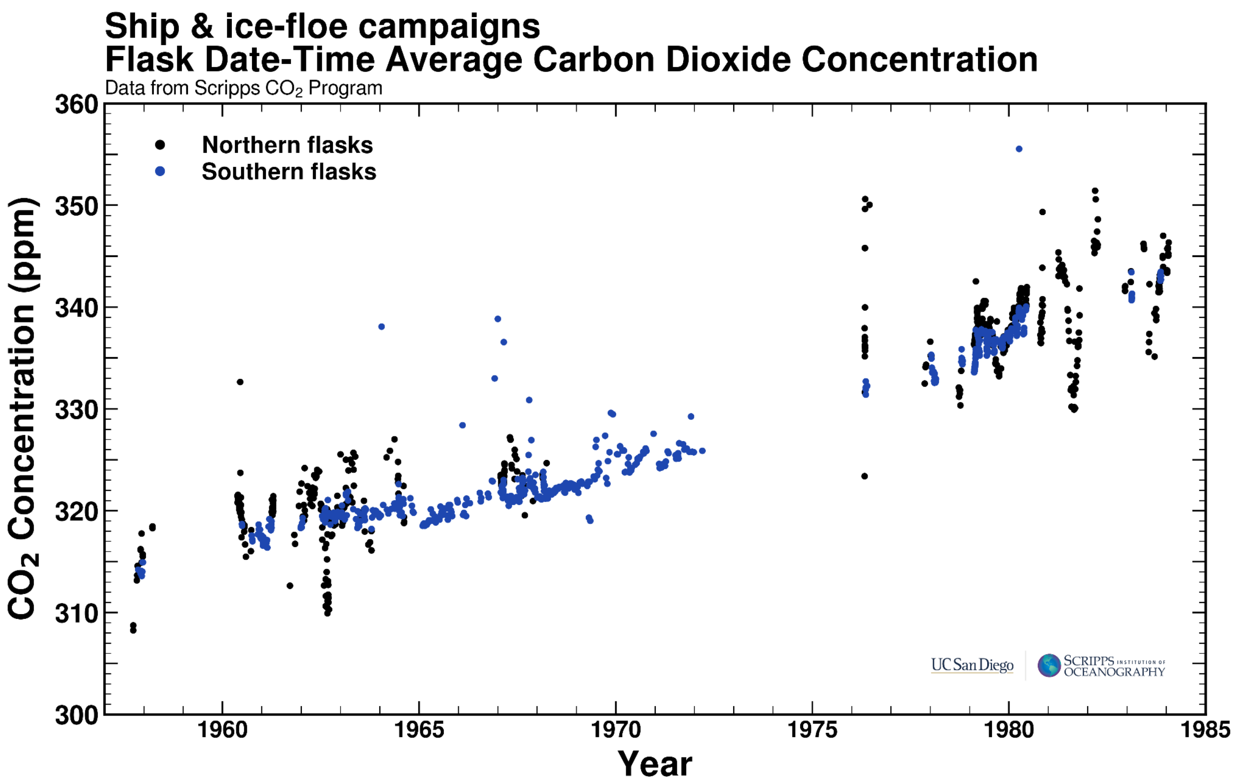

Figure 2. Flask date-time averages for all campaigns in this report on x08A scale with accepted flag values and within 3 std of mean.

Digital and paper data resources

In preparing these datasets, the following digital and paper data resources were available.

Digital campaign data. For this project we found digital raw data files on the group server in the directories of Tim Whorf, a member of C.D. Keeling's laboratory, in a folder named whorf_duc0/ship. These files have a naming convention of fli.<campaign> where <campaign> represents a 3 character abbreviation of each campaign, e.g. the file fli.arl_1 contains raw flask values for the Arlis campaign. Prior to finding these files, we were under the impression that all the early campaign digital records had been lost due to a failure of an early

VAX group server with limited backups. With these raw digital files, we were able to supersede the need to rely on optical character recognition (OCR) digital versions of paper data records from the so-called Bollenbacher Brown Book" (Bollenbacher 1983). The campaign flask files found on the group data server included more ship and ice-floe campaign data than the values in the Bollenbacher Brown Book.

Each of these digital raw data files contained a table with the following data columns: flask ID, flask volume (2, 3, or 5 L), sampling date and time (local or UTC), latitude, longitude, observer initials, CO_2 in I index to 2 decimal places, analysis date, flag of flask measurement order, reference gas report number, campaign abbreviation, field sheet number, and analysis sheet number. The flag of flask measurement order was represented as a two digit number where the second digit represents the total number of CO_2 measurements and the first digit represents the first, second, third, etc. measurement. (e.g. 13, 23, or 33). The analysis sheet number is an internal numbering system of paper sheets recording the analysis to convert APC analyzer response to I index values. Index values are linear to APC analyzer response.

Fortran program and correction files.

This report's processing made use of a Fortran program, qflcor.for (Keeling 1986a), that is a standard tool used in the Scripps program for the reduction of CO_2 data from I index values to CO_2 mole fraction values on a calibration scale. This program also takes two input files detailing various corrections that are variable over time, such as period corrections to I index values (pecor.dat) and manostat pressure corrections (shpres.dat). For this report, the latest version of pecor.dat, created in 1987 (Keeling 1987), was used which updates period corrections defined in Keeling 1984a. The Keeling (1986b) report used the earlier 1984 version of pecor.dat. We also had available an earlier Fortran version of qlfcor.for that dated from 1985. This Fortran program was not used to generate the final output tables, but was used to verify its calculations duplicated data presented in the Keeling (1986b) report. See appendix A and B for more information about the corrections applied and the Fortran program described.

Field data sheets. We had available field data sheets that were created during campaign flask sampling. See appendix F for an example of a full sheet. These sheets were used to determine if dates and time were local or GMT in the digital raw data files. The field data sheets during each campaign were used to indicate the ship, flask ID, flask volume, sample date, sample time, time zone (local or GMT), observer name, latitude, longitude, weather conditions, and comments on any sampling problems. Field data sheets were found for all campaigns except for Downwind (DWN). For DWN, we were able to locate summary data sheets that included whether local or GMT dates and times were recorded. As part of a previous project, field data sheets were scanned into a PDF format, e.g. the field data sheets for the ice floe A campaign were scanned and saved as a PDF to ice_floe_a_flask_sample_field_data_1957.pdf.

Summary tables. For some, but not all campaigns, we had available summary tables on paper sheets listing CO_2 Index values and calculated CO_2 mole fraction values. See appendix G for an example summary table. The tables were in handwritten or typed form. All of the located summary tables had at least the following information: flask ID, date and time (local or GMT indicated), latitude and longitude, I index in ppm. Some tables also included CO_2 values on various calibration scales, flask averages and daily flask averages. The summary tables often included asterisks next to flask index values indicating whether to exclude or include flask measurements in final results. It wasn't always noted why the values were rejected.
The paper summary tables were used to determine which flasks were peremptorily excluded, and for date/time information for DWN. By comparing these summary data tables with the digital raw data files, we were able to determine that these contained essentially the same information, although the paper records also contain hand-written notes marked in the columns. As part of this project, summary tables were scanned to produce PDF files, e.g. the ice floe A and B campaign summary table sheets were saved as a PDF to ice_floe_a_b_co2_indices_1957-1958.pdf.

Keeling 1986b report. We had available a paper version of the Keeling et al (1986b) report which contained flask averages data tables for various campaigns with flags marked on the tables as described in the 1986b report. The relevant campaign tables from this report were extracted using OCR to retrieve the flags and these flags are included as an additional column in our updated flask averages data table. Flag columns in the flask averages data table can be used to facilitate comparisons with data from earlier publications (e.g. Keeling et al., 1989b, Keeling et al., 2011). The Keeling (1986b) report was converted to a PDF and named keeling_1986_report_w_ship_tables.pdf.

Methods to prepare data resources for analysis

We checked the digital raw campaign data files against the corresponding field data sheets to make sure the time zones matched and to check if there were any human transcription errors. The digital raw data files occasionally had rows with an asterisk (*) next to some values. The significance of this asterisk was unclear, but we interpret it as a flag to exclude the row. Entries were modified if the latitude or longitude was missing the hemisphere designation (N or S, E or W) which we were able to determine from neighboring values. Rows with missing latitude and longitude values were excluded. Rows with out- of-range latitude or longitude (e.g. > 90 for latitude or >180 for were also excluded. Times of 1200A were changed to 0000 and times of 2400 were changed to 23:59 when reading in X values in later processing (using the Matlab script lmm_cdflreadx.m).

Production of the Campaign Data Set

We processed each raw digital campaign file separately and concatenated the results into the flav_all_cruises.csv and fldav_all_cruises.csv files.

We checked the I index values to fix any human entry errors from paper sources to digital format, and we removed any rows with missing information needed to process the data. We modified earlier Fortran code, qflcor.for, to create the program ship_qflcor08a_pub.f, which we used to convert each Index value to a CO_2 concentration on the x08A scale. The source for our modification was a version of qflcor.for (named qflcor08a_pub.f) that had been used previously to place aircraft data on the 08A scale (Piper 2012). The code was modified to include additional corrections for 2-liter flasks for all campaign data.

The output of the Fortran program was further processed with a series of MATLAB scripts to calculate flask averages from single or multiple measurements on individual flasks, and then flask date-time averages were calculated from flask averages. Flasks collected within a window of 10 minutes were treated as replicates for the purpose of calculating date-time averages. The window of 10 minutes was chosen to account for slight variations in flask sampling times for a group of replicate measurements. The 10 minute window was also chosen to be small enough to resolve small differences in lat and lon due to ship movement. From examining the campaign raw flask files, the majority of replicate flasks are taken in rapid succession (< 10 min). Flagging and calculating the flask averages and flask date-time averages is discussed below.

Converting to the x08A scale

The Fortran program named ship_qflcor08a_pub.f, applies a series of corrections to the starting I Index values and converts them to CO_2 mole fractions. This program takes as input the I Index value, flask volume size, reference gas analysis date, and the number of the analysis sheet where the index values were recorded. The analysis sheets were not used as part of this workup, but the recorded number of the sheet is used when applying period corrections and manostat pressure corrections. These corrections are read from two supplemental data files, shpres.dat for manostat pressure corrections and pecor.dat for various instrument corrections over period ranges. Hardwired into the Fortran program is a correction based on flask volume that is used for certain campaigns using 2 liter flasks. The Fortran program also reads in a file for flask analysis flags, but this file is empty for each campaign. Empty flag files were used in keeping with the flag files used for the Keeling (1986b) report which were empty. See the Appendix for more information.

Date/time conversion

Any stations using local time were converted to UTC time with a Matlab routine named timezone.m which takes in a longitude and returns the offset needed to convert local time to UTC time. The time conversion was done separately for both flask average and flask date-time averages.

Flagging

We followed the same flagging procedure as Keeling (1986b). This procedure combines many different types of flags, including flask average flags, date-time average flags, and peremptory ship report flags (from Keeling (1986b) indicating whether a measurement value is accepted or rejected.

The flask average output file (flav_all_cruises.csv) contains four flag columns in total. The first flag column indicates if the measured flask values were accepted to create the average and the second indicates if the flask average was accepted or not in the (subsequent) date-time average calculation. The third flag column indicates if a flask average was used in the 1986b ship report and if so also indicates the flag from that report, and the fourth indicates if the flask average was used in the 2011 monograph (Keeling et al, 2011).

The flask date-time average output file (fldav_all_cruises.csv) contains one processing flag column indicating if the value is accepted due to using accepted flask averages in the calculation.

Following the Keeling et al. (1986b) methods, we require flasks to fall within a maximum range (replicate cutoff value) to be accepted into the date-time average. We thus used a replicate cutoff of 0.4ppm for all campaigns except FGGE (0.25ppm) and STN (0.6ppm). For any campaigns not mentioned in the 1986b report, we used a replicate cutoff of 0.4ppm except the ice-floe campaigns, ICA and ICB, where we used a replicate cutoff of 1.2ppm in order to avoid excluding data, since there was so little data.

Except for the two information flags in the flask average file, all flagging was done following existing procedures. Rather than summarizing, we simply quote from previous reports detailing these procedures:

Explaining the basis of the 0.4 ppm cutoff (Keeling et al, 1984b):
"On the basis of a study of the statistical dispersion of differences between flask analyses obtained on a single day and analyzed by a single laboratory, we determined that most blunders in sampling and in analysis are eliminated by rejecting pairs of analyses which do not agree in X82 Mole fraction to within 0.40 ppm. Except for a few instances, flask pairs only are available for this screening, and in this case both analyses were rejected if they failed to pass the 0.40 ppm criterion. If three or more flask samples were obtained on a given day and analyzed by a single laboratory, then all such samples agreeing within 0.40 ppm of the lowest X82 mole fraction were kept, and those of greater difference rejected. If none agreed with the lowest then, as with pairs, all were rejected."

Explaining how the cutoff was applied (Keeling et al., 1986b):
"Rejection for poor replicate flask agreement: For pairs of samples of air obtained by exposing evacuated glass flasks consecutively, the daily average is flagged if the analyses differ by more than 0.40 ppmv. If three or more flasks were exposed together, each analysis was compared with the lowest value, thus treating the set as multiple pairs. All analyses differing by more than 0.40 ppmv from the lowest value were discarded. If no pair was found to agree within 0.40 ppmv, the average of all analyses is listed with a flag. If one or more flask analyses agree within 0.40 ppmv with the lowest concentration, these and the lowest value were averaged and appear in the table without a flag."

Explaining methods for peremptory flagging (Keeling et al., 1986b):
"In two cases, data flagged according to the 0.40 ppmv cutoff parameter were accepted back into the data set. Data for air over South Pacific ocean on Monsoon campaign were obtained in a region where little variation in CO_2 concentration is expected owing to the vigorous winds and lack of nearby sources or sinks capable of altering the concentration locally to a significant extent. Thus the data could be considered to belong to a single statistical set. Since the rejected flask analyses,

with one exception, appeared to be consistent with the single pair agreeing within 0.40 ppmv, these analyses could be expected to produce an average statistically more valid than that of a single pair of observations. At Weathership 'N', at 30°N in the North Pacific ocean, a large number of analyses were available at a single location, again providing a basis for considering these data as a single statistical set. The rejection criterion was relaxed to 0.60 ppmv. Two pairs were rejected peremptorily because the samples were stored for two years before analysis."

References

Bolin, B. and C.D. Keeling. Large-Scale Atmospheric Mixing as Deduced from the Seasonal and Meridional Variations of Carbon Dioxide. *Journal of Geophysical Research.* 68 (1963): 3899-3920.

Pales, J.C. and C. D. Keeling, 1965. The concentration of atmospheric carbon dioxide in Hawaii. Journal of Geophysical Research, 70, 6053-6076.

Keeling, C.D., T.B. Harris, and E.M. Wilkins, 1968. Concentration of atmospheric carbon dioxide at 500 and 700 millibars. Journal Geophysical Research 73 (14), 4511-4528.

Keeling, C.D. R.B. Bacastow, A.E. Bainbridge, C.A. Ekdahl, P.R. Guenther, and L.S. Waterman, 1976. Atmospheric carbon dioxide variations at Mauna Loa Observatory, Hawaii. Tellus 28, 538-551.

Bacastow, R.B., C.D. Keeling, P.R. Guenther, and D. J. Moss, 1983a. Scripps reference gas calibrating system for carbon dioxide in nitrogen standards: Revision of 1980. A report prepared for the Environmental Monitoring Program of the World Meteorological Organization, Scripps Inst. of Oceanography, La Jolla, CA, 64 pp.

Bacastow, R.B., C.D. Keeling, P.R. Guenther, and D. J. Moss, 1983b. Scripps reference gas calibrating system for carbon dioxide in air standards: Revision of

1981. A report prepared for the Environmental Monitoring Program of the World Meteorological Organization, Scripps Inst. of Oceanography, La Jolla, CA, 33 pp.

Bollenbacher, A., 1983. Flask station data files, (compilation of flask data for land stations, ship cruises, and aircraft sampling), binder of computer line-printer output, Scripps CO2 Program, Scripps Institution of Oceanography, La Jolla, CA, 111 pp.

Keeling, C.D., 1984a. Adjustments to Applied Physics infrared analyzer data to allow for differences in response of the various detectors used (Draft 16, September 4, 1984), 71 pp. plus 4 pages of typed inserts dated 2 December 1985 and 15 February 1987. Keeling Archives at Scripps Inst. of Oceanography Library, accession no. 2006-18, Box 136.

Keeling, C. D., T. P. Whorf. and C. S. Wong, Weather station 'P' carbon dioxide project report, 100 pp., Scripps Inst. of Oceanography, La Jolla, Calif., 1984b.

Keeling, Charles D., Alane F. Carter, and Willem G. Mook. Seasonal, Latitudinal, and Secular Variations in the Abundance and Isotopic Ratios of Atmospheric Carbon Dioxide 2. Results from Oceanographic Cruises in the Tropical Pacific Ocean. *Journal of Geophysical Research.* 89 (1984c): 4615-4628.

Keeling, C.D., P.R. Guenther, and D.J. Moss, 1986a. Scripps reference gas calibration system for carbon dioxide in air standards: Revision of 1985. Environmental Pollution, Monitoring, and Research Programme Report Series No. 42 of the World Meteorological Organization (Technical Document WMO/TD---No. 125), 76 pp. with addendum.

Keeling, C.D., P.R. Guenther, and T.P. Whorf. An Analysis of the Concentration of Atmospheric Carbon Dioxide at Fixed Land Stations and over the Oceans based on Discrete Samples and Daily Averaged Continuous Measurements. Carbon Dioxide Project Report, 1986b.

Keeling. C.D., 1987. Review of adjustment report, handwritten notes in folder labeled "Adjustment report 1987", dated 15, 17 February 1987, Keeling Archives at Scripps Inst. of Oceanography Library, accession no. 2006-18, Box 136.

Keeling, C.D., R.B. Bacastow, A.F. Carter, S.C. Piper, T.P. Whorf, M. Heimann, W.G. Mook, and H. Roeloffzen. A Three Dimensional Model of Atmospheric CO2 Transport Based on Observed Winds: 1. Analysis of Observational Data. *Aspects of Climate Variability in the Pacific and the Western Americas.* Ed. Peterson, David H.. Washington, DC: American Geophysical Union, 1989a. 165-236.

Keeling, C.D., S.C. Piper, and M. Heimann A Three Dimensional Model of Atmospheric CO2 Transport Based on Observed Winds: 4. Mean Annual Gradients and Interannual Variations. Aspects of Climate Variability in the Pacific and the Western Americas. Ed. Peterson, David H.. Washington, DC: American Geophysical Union, 1989b. 305-363

Keeling, C.D., P.R. Guenther, G. Emanuele, A. Bollenbacher, and D.J. Moss, 2002. Scripps reference gas calibration system for carbon dioxide-in-nitrogen and carbon dioxide-in-air standards: revision of 1999. A report prepared for the Global Environmental Monitoring Program of the World Meteorological Organization, Scripps Institution of Oceanography, 77 pp.

Keeling, Charles D., Stephen C. Piper, Timothy P. Whorf, and Ralph F. Keeling. Evolution of natural and anthropogenic fluxes of atmospheric CO2 from 1957 to 2003. *Tellus B*. 63 (2011): 1-22.

Piper, S.C., 2012. Scripps Early Aircraft CO_2 Dataset, Scripps CO_2 Program, Scripps Institution of Oceanography, La Jolla, CA. Retrieved from https://scrippsco2.ucsd.edu/assets/supplemental/aircraft/readme-aircraft-data.pdf

Weiss, RF, Van Woy FA, Salameh PK. 1992. Surface water and atmospheric carbon dioxide and nitrous oxide observations by shipboard automated gas chromatography : results from campaigns between 1977 and 1990. Scripps Institution of Oceanography Reference Series. :144., La Jolla, Calif.: Scripps Institution of Oceanography, University of California, San Diego

Appendix

A. Corrections applied for the x08A scale

Calculating CO_2 values on the x08A calibration scale involves corrections for the manometer, period, pressure, flask volume, revised manometric determinations, flask storage conditions, and carrier gas (N2 or air). The Scripps CO_2 program has retained computer programs for automatic reduction of data collected throughout the program history, extending back to the 1960s. See Keeling 1986a for an overview of the Fortran program used to calculate flask CO_2 values on a calibration scale and a discussion of the corrections applied. The computer programs convert measured I Index values to mole fraction values and have been modified over the years as corrections were discovered due to equipment and flask changes. Each calibration scale adds new corrections. The CO_2 values in Keeling et al. (1986b) are on the x85 scale and were calculated in 1986. Relative to the program used from the Keeling 1986b report, the program used here differed by including the latest manometric corrections and including an updated version of the percor.dat file (for period corrections) based on the update in Keeling (1987). The corrections are described below and the Fortran correction routines are described in Appendix B.

1) 1959 manometer correction

Data initially were worked up as "index values" (referred to as I index) where the index is linear in APC analyzer response. Manometric calibrations from 1959-1961 were used to produce a new provisional manometric mole fraction scale also linear with the APC response, called the "adjusted index" or "J index". The adjusted index J is calculated from the I index as follows:
$J = (I - 311.51)*1.2186 + 311.51$

2) Two liter correction

Air samples were taken in 2, 3, and 5 liter flasks. Two liter flasks tend to produce higher values of CO_2 due to a storage effect (Keeling, 1984a, Keeling 1984b, Keeling 1986b). The correction to the 2 liter flask data is applied by reducing the original J index values by 0.12 ppm.

3) Period correction

Detectors in the Scripps APC analyzer were repaired or replaced several times from 1958 to 1968 producing a change in the response of the analyzer. Corrections were formulated by Keeling (1984a, 1987). In Keeling (1986b), the 1984 period correction file, pecor.dat, is used with the x85 calibration scale, and for this 2024 report, the updated 1987 period correction file is used with the x08A calibration scale.

4) Pressure correction

A manostat pressure correction is applied for ranges of analysis dates from 1957 to approximately March of 1964. These pressure corrections are read in by ship_qflcor08a_pub.f from an ascii file named shpres.dat and indexed to reference gas analysis sheet numbers (shpres = sheet pressure). The pressure values are from a sample cell of NDIR analyzer. For analysis sheet numbers not included in the shpres.dat file, the full atmospheric pressure of 760.46 is used. Analysis dates on the analysis sheets do not correspond with flask sampling dates, e.g. dates can be analyzed over a year after the flask sampling date.

5) Storage correction

From a comment in the 1985 version of the qflcor Fortran program: Flasks stored for abnormally long times between sampling and analysis showed a small increase in CO_2. This correction is applied only to data from Fanning and Christmas Islands and Mauna Loa, not to the ship data.

6) Drift correction (subroutines CORR1, CORR2, and CORR3)

Correction for drift in the reference gas system, as formulated for periods prior to 1983 (Bacastow et al., 1983a, Keeling et al. 1986).

7) Manometer volume correction (subroutines CORR4 and CORR5)

Redetermination of volumes in the constant volume manometer required the original results for dates prior to 1985 to be multiplied by a constant factor 1.000503 (Keeling et al., 2002).

8) Carrier gas correction (subroutine CORR5)

Ship samples were analyzed with CO_2-in-N_2 reference gasses. The difference in the carrier in the samples (air) and reference gasses (N_2) produced CO_2 values that are about 1% too low. With the sample specified to be of type AIR (A), subroutine CORR5 is called and produces XAIR, which is CO_2 corrected for the carrier gas effect (Keeling et al., 2002).

In CORR5, additional air cubic routines are added as the program gets updated every few years. For the x08A scale, the 1985 air cubic routine, ACUB85, which was used in Keeling 1986b was modified along with adding additional cubic routines up to 2008.

B. Fortran program to convert raw index values to the x08A scale

The program ship_qflcorx08A_pub.f calculates CO_2 mole fractions from APC analyzer index values according to the Scripps "x08A" CO_2 calibration scale, for either nitrogen or natural-air CO_2 reference gasses. See Keeling 1986a for an overview of a 1985 version of the Fortran program. For this ship report, natural-air has been chosen for the program. Comments are included related to updates of the calibration system since 1985 and to changes in the computing program. This version of the program is designed to calculate the mole fraction from input of the Scripps I index, the date of analysis on the APC analyzer, and indication of the type of the gas sample. The program applies several corrections discovered since publication of the data in 1968. The program is essentially the same as CORRECT99A.F documented in Keeling et al. (2002). Here we document the points in the program where corrections are applied. In the program, the I index is referred to as DEX and the J index CMAN59. Depending on the date of analysis and type of gas specified, the program diverts to the appropriate subroutines.

SUBROUTINE CALDAY
Central dates for the calibration periods from 1960 to 2008 are listed here.

SUBROUTINE CALxx
The portion of the program that applies various calibration equations for specified time periods.

SUBROUTINES CORR1 to CORR3
These subroutines carry out calculations accounting for drift in the reference gas system, as formulated for periods prior to 1983.

SUBROUTINE CORR4
Cubic equations are applied to the data, beginning with the 1980 calibration, for nitrogen reference gasses. Linear interpolations are performed for periods between central dates of calibration periods after 1983.

SUBROUTINE CORR5
Cubic equations are applied to the data, beginning with the 1983 calibration, for natural-air gasses. Linear interpolations by date are done for periods between central dates of calibrations.

CUBIC FUNCTIONS FOR CO2-IN-AIR and CO2-IN-N2

Calibration equations applicable to central dates of each calibration are given as functions named ACUBYY (for example, ACUB85) for natural-air reference gasses and CUBYY for nitrogen reference gasses. Cubics prior to 1985 are reported in Keeling et al. (1986a), and cubic functions for 1985 to 1999 in Keeling et al. (2002). Functions after 1999 were developed similarly to those in 1999.

C. Structure of unprocessed data files (fli.sta)

The first row contains the three letter abbreviation of the campaign. The rest of the rows are formatted as follows:

Column number	Size	Type	Description
1	5 character	string	Flask identifier
2	1 digit	integer	Flask size in liters
3	6 digit	integer	Sample date YYMMDD
4	4 digit	integer	Sample time HHMM
5	2 digit	integer	Latitude degrees
6	2 digit	integer	Latitude minutes
7	1 character	string	Latitude direction (N/S)
8	3 digit	integer	Longitude degrees
9	2 digit	integer	Longitude minutes
10	1 character	string	Longitude direction (E/W)
11	3 character	string	Observer initials
12	6 digit	real	I Index value
13	6 digit	integer	Analysis date YYMMDD
14	2 digit	integer	Flag for the measurement order
15	3 digit	integer	Reference gas report number
16	3 character	string	Station name abbreviation
17	3 digit	integer	Field sheet number
18	4 digit	integer	Analysis sheet number

The analysis sheet number is required but the field sheet number is not. The analysis sheet number is the number on a paper record containing the analyzer results for a flask.

Column 14, the flag for the measurement order, represents the order of the flask measurement and the total flask measurements made, .e.g. if one flask ID has 3 measurements, the flag would be 13, 23, and 33 which means 1st of 3, 2nd of 3, 3rd of 3 measurements.

D. Program folder structure

The directory structure is as follows. There is a parent folder named flask_processing and subfolders named cdrgflask_fortran, cdrgflask_matlab, and flasks08A. The executable bash script run_matlab_processing.sh which creates the flask average and flask date-time averages is in the folder flasks08A. The Fortran program ship_qflcor08a_pub.f, which converts I index into CO_2 mole fractions on the x08A scale, and its compiled format ship_qflcor08a_pub.x are in the folder cdrgflask_fortran. The MATLAB scripts are in the folder cdrgflask_matlab. The raw data and supporting files, such as flagging, index corrections, and file headers, needed for the Fortran and MATLAB scripts are in the subfolder input of the flasks08A folder. The folder named data holds intermediate files created by the program. The output of the program of flask average, flav_all_cruises.csv, and flask date-time average, fldav_all_cruises.csv, files are in the folder named output. The entry bash script run_matlab_processing.sh calls the MATLAB script lmm_cdflmain.m.

E. Programs to create flask average and flask date-time averages

To create the flask average, flav, and flask date-time average, fldav, files on the x08A calibration scale for the campaign raw flask files, execute the bash script named run_matlab_processing.sh from inside the folder flasks08A. The MATLAB scripts called by the bash script call both the executable Fortran program ship_qflcor08a_pub.x to convert flask raw index values into CO_2 mole fractions and other MATLAB scripts that calculate flask averages (flav) and flask date-time averages (fldav) and save them to files for each campaign and for campaigns concatenated together. Input data files have a naming schema of fli.sta where sta is a 3 letter abbreviation of the campaign (see Table 1).

F. Detailed descriptions of MATLAB scripts and supporting files

MATLAB files

The matlab programs were contained in a folder named cdrgflask_matlab. This folder contained the following files:

lmm_cdflmain.m: Main Matlab script to process data files.

lmm_convert_index_to_x_scale.m: Matlab script to call Fortran program ship_qflcor08a_pub.f converting index values to x08A values.

lmm_calc_flask_average.m: Matlab script to calculate flask average.

lmm_cdflsetflaskflags.m and **lmm_cdflsetflagperiods.m**: Matlab scripts to apply peremptory flask average flags.

lmm_calc_datetime_average.m: Matlab script to calculate date-time average.

lmm_convert_local_to_utc_time.m: Matlab script to convert local times to UTC.

lmm_concat_all_flav2.m and **lmm_concat_all_fldav2.m**: Matlab scripts to concatenate individual data files into flav_all_cruises.csv and fldav_all_cruises.csv

Data, flags, headers, and correction files

Support files are stored in the input folder and contain raw flask files, flagging files, correction files needed for the x08A calibration scale, campaign time zones, and file headers for the generated flav and fldav files.

fli.sta: starting flask CO_2 campaign data in I index

flflag.sta: ascii files to hold measurement flagging (empty for processing but needed for the program)

sta_period_bad_flags.csv: peremptory station flags during time period

sta_manual_flask_flags.csv: peremptory station flags

sta_shp86_flask_flags.csv: station flagging used in the 1986 ship report

ica_flask_in_2011.csv and **icb_flask_in_2011.csv**: Flagging indicating ICA and ICB flasks that appear in the 2011 paper

station_time_zones.csv: ascii file listing stations with UTC times

headers: folder of header files to create output headers

pecor.dat: ascii file of period corrections used by ship_qflcor08a_pub.f where ranges of analysis sheet numbers in the first two columns are indexed to corresponding Index value corrections in the third column. The analysis sheet numbers refer to reference gas analysis sheets where measurement results for flasks were noted and the sheets numbered. So a sheet number represents an analysis date. Corrections were formulated by Keeling (1984a, 1987).

shpres.dat: ascii file listing pressure of a sample cell of NDIR analyzer indexed to analysis sheet numbers (shpres = sheet pressure) used by qflcor08a_pub.f. For analysis sheet numbers not listed in this file, the full atmospheric pressure is used of 760.46. This file is the same for both the analysis in Keeling (1986b) and this 2024 report.

Output Files

Processed files are in the folder output and contains the flav and fldav campaign data in UTC.

flav_sta: station flask averages files after UTC time zone correction

fldav_sta: station flask date-time average files after UTC time zone correction

flav_all_cruises.csv: concatenated file of all station flask average files after UTC time zone correction

fldav_all_cruises.csv: concatenated file of all station flask date-time average files after UTC time zone correction

F. Example Field Data Sheet

Field data sheet from Monsoon Campaign on August 30th, 1960

VESSEL: ARGO
DATE: 30 Aug 60
CRUISE: MONSOON
TIME ZONE: +9
SAMPLE FLASK NOS.: 113 + 114

CARBON DIOXIDE PROGRAM
ATMOSPHERIC SAMPLING DATA SHEET

SHEET NO. 3

Local Time (Hr.Min.) 1920 (7:20 p.m.)

Latitude (Deg.) N/S N - 20° 14'

Longitude (Deg.) W/E W - 134° 52'

Air Temp. (°F) 74.5

Wet Bulb Temp (°F) 61.3

Surface Water Temp. °F °C 21.8

Barometer: 30.00

Weather: 00 - clear.

Cloud Type: 8 - cumulus

Cloud Amount: 1 - 1/10 or < 1/10

Visibility: 8 - 30 miles, good.

Sea (BT Log; Table 7) 3 - slight

Ship's Head (Deg.) 231°

Ship's Speed (Knots) 12.5

Wind Direction: Relative True NE.

Wind Speed: Relative True 15 knots.

Remarks: wind following astern of ship - very light airs in vicinity of flying bridge as result. Possibility of contamination.

Analyzed May 11, 1961

G. Example Summary Table Sheets

Typed summary table for Monsoon Campaign with notations

MONSOON CRUISE - FLASK SAMPLE INDEX VALUES

Col: 1 Sample Sheet No.	2 Flask Volume (liter)	3 Date Exposed	4 Hour	5 Flask No.	6 Individual	7 Average	8 Lat.	9 Long.	10 Observer	11 Date Anal.	12 Sheet No.
		1960								1961	
1	1.8	Aug. 27	1130	109	308.37						165
				110	309.04	308.~~8~~70	30.2 30-15N	120-37W P	C	May 11	165
2	1.8	Aug. 28	2320	111	309.90						166
				112	309.42	309.~~7~~66	25.2 25-11N	128-05W	C	May 11	166
3	1.8	Aug. 30	1920	113	310.95						166
				114	310.47	310.~~80~~71	20.2 20-14N	134-52W	C	May 11	166
4	1.8	Sept. 1	1630	115	313.41 &						194, 177
					312.86						
				116	317.65 &						
					317.17 **	313.~~22~~14 *	15.0 15-00N	141-47W	C	Aug. 25	194, 177
5	1.8	Sept.21	0100	125	313.05						165
				126	312.86	312.96 ~~313.04~~	9.1 9-06N	166-26W	C	May 11	165
6	1.8	Sept.22	2305	127	314.39						165
				128	314.96	314.~~76~~68	5.0 5-0 N	171-28W	C	May 11	165
7	1.8	Sept.25	0845	129	314.77						165
				130	314.48	314.~~72~~63	0.0 0-0	180-0	C	May 11	165
8	1.8	Sept.28	0540	131	314.20						165
				132	314.20	314.2~~8~~0	5.1 5-05S	176-23E	C	May 11	165
9	1.8	Sept.30	1851	173	317.74						194
				174	314.33	314.~~42~~33 *	9.0 9-04S	170-52E P	C	Aug. 25	194
10	1.8	Oct. 4	1500	175	313.96						194
				176	313.78	313.~~96~~87	14.9 14-56S	153-46E I	C	Aug. 25	194
11	1.8	Oct. 5	1600	177	313.69						194
				178	313.78	313.~~82~~74	15.0 15-0S	150-16E	C	Aug. 25	194
12	1.8	Oct. 6	0745	179	313.~~8~~60						194
				180	349.42	313.6~~9~~0*	16.2 16-10S	147-14E	C	Aug. 25	194
13	1.8	Nov. 22	0850	101	315.15						164
				102	314.20	314.~~76~~68	10.5 10-30S	98-59E	C	May 10	164

MONSOON CRUISE - FLASK SAMPLE INDEX VALUES

Col: 1 Sample Sheet No.	2 Flask Volume (liter)	3 Date Exposed	4 Hour	5 Flask No.	6 Individual	7 Average	8 Lat.	9 Long.	10 Observer	11 Date Anal.	12 Sheet No.
		1961								1961	
59	5.0	Apr. 14	0850	125	316.34	44	24.3				193
				126	316.53	316.52	24-20N	126-31W	H	Aug. 24	193
60	5.0	Apr. 15	0925	37	316.73	0	26.3				192
				38	316.46	316.63	26-18N	124-34W	H	Aug. 23	192
61	5.0	Apr. 15	2020	39	317.01	87	27.6				192
				40	316.73	316.96	27-36N	122-42W	H	Aug. 23	192
62	5.0	Apr. 16	0840	41	317.29	0	29.2				192
				42	317.10	317.23	29-11N	121-01W	H	Aug. 23	192
63	5.0	Apr. 16	2100	43	316.00	0	30.0				192
				44	316.00	316.03	30-00N	120-07W	H	Aug. 23	192
64	5.0	Apr. 17	0915	45	316.62	80	31.4				193
				46	316.99	316.88	31-22N	118-42W	H	Aug. 24	193
65	5.0	Apr. 17	1805	47	319.00	26	33.6				193
				48	317.26	317.34 *	33-34N	118-36W	H	Aug. 24	193

* Average represents one sample
** Previously analyzed June 7, 1961, 2 values

Observers:
- C - Coatsworth
- W - Waterman
- H - Harris